POOR QUALITY

PATENT SPECIFICATION

1,139,450

NO DRAWINGS

1,139,450

Inventors: PIETER ANTOINE GAUTIER, SIMON MOSTERT and HERMAN VERBRUGGE

Date of Application and filing Complete Specification: 27 Dec., 1967.
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Int. Cl.:—C 08 f 1/36

COMPLETE SPECIFICATION

Process for the preparation of a Catalyst-Forming

PATENTS ACT, 1949

SPECIFICATION NO. 1,139,450

The following amendments were allowed under Section 29 on 29 April 1969

Page 11, line 6, *for* "I-IV" *read* "I-VI"

Page 12, Table VII, fourth column, *for* "11" *read* "1"

THE PATENT OFFICE,
26 June 1969

D 115979/29

pulverulent mixtures thereof with small quantities of a rubbery copolymer of ethylene with propylene and pulverulent copolymers of ethylene or propylene with very small quantities of a second monomer, for example pulverulent copolymers of propylene with at most a few percent by weight of ethylene, also belong to the products which it is desired to prepare by means of the catalyst components according to the invention. The percentage of material present in the envisaged polymer powders that is soluble in boiling diethyl ether should in general be less than 10% by weight and preferably at most 3% by weight.

The invention relates not only to the preparation of the said catalyst component but also to this component itself or a catalyst composition which contains one or more of these components. The scope of the invention is further extended to include the above-men-

surface and size as a result of which this component is capable of forming during the polymerization polymer particles which ultimately yield polymer powders having the improved properties envisaged.

The stirring power is determined via measurement of the torque of the driving motor and the speed of the impeller as described by J. H. Rushton, E. W. Costich and H. J. Everett in Chemical Engineering Progress *46* (1950) pages 395—404 and 467—477.

By specific stirring power is understood the stirring power in Watt per m^3 of reactor charge.

The highest temperature at which the mixture is heated and the time during which this temperature is maintained depend on the $TiCl_3$-modification which is desired in the catalyst component to be prepared. As long

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Int. Cl.:—C 08 f 1/36

COMPLETE SPECIFICATION

Process for the preparation of a Catalyst-Forming Component suitable for Polymerizing α-Olefins to Powders with improved properties

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the preparation of one or more catalyst components from titanium tetrachloride and diethyl-aluminium monochloride, specifically catalyst components by means of which α-olefins with at most six carbon atoms can be polymerized to a polymer powder having improved bulk density as well as improved flow properties.

The invention relates in particular to the preparation of a catalyst component of the said type which is suitable for homopolymerizing ethylene or propylene to the said polymer powders. Preferred is a polymer powder of isotactic polypropylene. However, pulverulent mixtures thereof with small quantities of a rubbery copolymer of ethylene with propylene and pulverulent copolymers of ethylene or propylene with very small quantities of a second monomer, for example pulverulent copolymers of propylene with at most a few percent by weight of ethylene, also belong to the products which it is desired to prepare by means of the catalyst components according to the invention. The percentage of material present in the envisaged polymer powders that is soluble in boiling diethyl ether should in general be less than 10% by weight and preferably at most 3% by weight.

The invention relates not only to the preparation of the said catalyst component but also to this component itself or a catalyst composition which contains one or more of these components. The scope of the invention is further extended to include the above-mentioned polymerization and the polymer powders obtained thereby.

The process for the preparation of the envisaged catalyst component comprises (1) mixing diethylaluminium monochloride and titanium tetrachloride at a temperature below −5°C in a molar ratio within the range of 0.5:1 to 1.2:1 in a paraffinic diluent which is substantially free of oxygen, in a reaction vessel whose contents are stirred at a specific stirring power within the range of 50 to 2000 Watt/m^3 and (2) subsequently increasing the temperature of the mixture to at least +15°C whilst stirring is continued at a specific stirring power which is kept within the same range at least as long as the temperature is still below +15°C.

Preferably the temperature below −5°C is not lower than −100°C, temperatures within the range of −45°C to −5°C being most suitable.

Under the said conditions a $TiCl_3$-containing catalyst component is obtained which consists of particles having a particular shape, surface and size as a result of which this component is capable of forming during the polymerization polymer particles which ultimately yield polymer powders having the improved properties envisaged.

The stirring power is determined via measurement of the torque of the driving motor and the speed of the impeller as described by J. H. Rushton, E. W. Costich and H. J. Everett in Chemical Engineering Progress *46* (1950) pages 395—404 and 467—477.

By specific stirring power is understood the stirring power in Watt per m^3 of reactor charge.

The highest temperature at which the mixture is heated and the time during which this temperature is maintained depend on the $TiCl_3$-modification which is desired in the catalyst component to be prepared. As long

as the maximum temperature is only 15°C—70°C the β-modification is obtained which is already highly suitable for the preparation of solid ethylene polymers with good mechanical properties. However, if it is desired to use the catalyst component for the polymerization of propylene to isotactic polypropylene, the $TiCl_3$ present in that component should for the greater part consist of the γ-modification, which modification can only be formed at temperatures above 70°C.

With regard to the conversion of the β- into the γ-modification the general rule applies that at the higher temperatures for example in the range of from about 150°C to 200°C, it is possible to use shorter heating times than at the lower temperatures, for example in the range of from about 70°C to 150°C. Thus, at a temperature of 150°C—160°C a heating time of 1 hour may be sufficient, whereas heating to only 100°C often necessitates maintenance of this temperature for at least 20 hours.

Consequently, it is preferred to raise the temperature of the mixture from below −5°C to a value within the range of 70°C to 200°C and then to lower it to a temperature below 70°C, e.g. to ambient temperature, while stirring is continued at a specific stirring power which no longer needs to be within the range of 50 to 2000 Watt/m³ as soon as the temperature is above +15°C. As a rule, however, the specific stirring power will also be maintained within the said range of 50 to 2000 Watt/m³ even during the temperature increase to above +15°C. If desired, lower values may be used but preferably not as long as the temperature is still below approximately +45°C. In general there will be little reason at this stage for stirring at a higher specific stirring power than 2000 Watt/m³.

It is further advisable not to have baffles in the reaction vessel in which the mixing of $AlEt_2Cl$ and $TiCl_4$ is effected.

In this vessel it is preferred to use high-speed agitators which sweep a volume of less than 10% of the internal vessel volume and rotate with a tip speed of more than 0.5 m per second. The greatest preference is given to turbine stirrers.

In the preparation of the catalyst component the following conditions were also found to be of importance and consequently their use, either separately or in combination, is preferred:

1. During the mixing of $AlEt_2Cl$ and $TiCl_4$ in the temperature range above −45°C, i.e. between −45°C and −5°C, maintaining the selected dosing temperature at a substantially constant level and mixing the two reactants gradually in such a manner that the selected molar ratio $AlEt_2Cl$: $TiCl_4$ of between 0.5 and 1.2 is attained in at least one hour but not more than eight hours.
2. Within the temperature range of −45°C to +45°C, ensuring an average rate of temperature increase of at most 1.5°C per minute and preferably of at least 0.1°C per minute.
3. Mixing the $AlEt_2Cl$ and the $TiCl_4$ at a temperature of from −10°C to −40°C.
4. Cooling the reaction vessel, including its cover, to the temperature selected below −5°C before introducing the $AlEt_2Cl$ or the $TiCl_4$ into this vessel. Moreover, the reactant which is the first to come into contact with the reaction vessel can, if desired, be pre-cooled to the same temperature. These measures are especially important if the reactor contains remnants of catalyst component originating from a previous preparation.
5. First introducing all of the $AlEt_2Cl$ into the reactor and only then adding the $TiCl_4$.
6. Mixing the $AlEt_2Cl$ and the $TiCl_4$ in a molar ratio of 0.65 : 1 to 0.85 : 1, preferably approximately 0.75 : 1.
7. Using both the $AlEt_2Cl$ and the $TiCl_4$ in a concentration of more than 500 millimoles per litre, the $AlEt_2Cl$-concentration preferably being less than 1800 millimoles per litre. To the extent that $AlEt_2Cl$ and $TiCl_4$ are used in the form of a solution it will be clear that use is most preferably made of a solution in the paraffinic diluent in which the mixing is to take place. The highest degree of purity is recommended in particular for the $TiCl_4$.
8. Using as paraffinic diluent alkanes having 4—10 carbon atoms, for example n-butane, n-pentane, n-hexane, 2,2,4-trimethylpentane, n-decane, isomers of these hydrocarbons or mixtures of the said alkanes. The presence of aromatic hydrocarbons in the diluent should be avoided as much as possible while a significant amount of cyclo-aliphatic hydrocarbons in the diluent is also not very desirable. Furthermore, the most favourable temperature for mixing the $AlEt_2Cl$ and $TiCl_4$ depends to some extent on the nature of the selected alkane. Thus quite reasonable results are still obtained for example in normal decane at a dosing temperature of −10°C, whereas the use of 2,2,4-trimethylpentane or a mixture of octane isomers causes the results even at −20°C to be slightly less favourable than at −30°C.

With regard to the specific stirring power at which the $TiCl_3$-containing catalyst component is prepared it should be noted that at least as long as the temperature of the mixture is below +15°C, values of 80 to 800 Watt/m³ are as a rule preferred. It is also preferred to keep the stirring speed constant right from the beginning of the mixing step, again at least as long as the temperature of the mixture is below +15°C. Given a constant stirring speed, the specific stirring power

remains constant as long as there is no change in the liquid volume. Since during the mixing of the $AlEt_2Cl$ and the $TiCl_4$ the liquid volume increases, the specific stirring power drops accordingly.

Preferably the stirring conditions selected for the temperature range between +15°C and +70°C are equal to those which have to be used at temperatures below +15°C, i.e. the same range is preferably applied for the specific stirring power.

In certain cases it may be desirable at a temperature between +15°C and +45°C to raise the specific stirring power, if necessary beyond the said upper limit of 2000 Watt/m³ by increasing the stirring speed.

It has proved advantageous to keep the temperature of the mixture for at least 45 minutes and preferably for at least two hours at a value between +15°C and +45°C and most preferably between +25°C and +45°C.

The subsequent heating of the mixture at a higher temperature, in particular at a temperature above 100°C, may take place in the same reaction vessel, with stirring, provided this vessel is capable of withstanding elevated pressure. It is also possible, however, to use two stirred reactors one after the other, in which case at least the second reactor is an autoclave suitable for carrying out the heating to above 100°C. The dimensions of this second reactor as well as of the stirrer present therein need not be the same as those of the reaction vessel in which the mixing of the $AlEt_2Cl$ and the $TiCl_4$ takes place. The type of stirrer in the second vessel may also differ from that used in the first vessel.

In the preparation of the $TiCl_3$-containing catalyst component $AlEtCl_2$ is almost invariably formed according to the reaction:

$$TiCl_4 + AlEt_2Cl \rightarrow TiCl_3 + AlEtCl_2 + Et.$$

The extent to which this reaction proceeds is dependent, inter alia, on the selected molar ratio of the reactants to be mixed. Since the activity of the catalyst component is impaired by the presence of this $AlEtCl_2$, it is recommended either to remove this aluminium compound from the mixture, for example by careful washing with diluent, or to render it harmless by conversion into $AlEt_2Cl$ or a complex. These conversions are preferably performed at the end of the production process, i.e. when the conversion of the catalyst component into the γ-modification (provided of course that this modification is desired) has already taken place. To the extent that it is desired to complex the $AlEtCl_2$, preference is given to complexing with the aid of a Lewis base, such as for example an ether or an amine. Thus, very good results are obtained if dibutyl ether is used as an ether. The conversion of $AlEtCl_2$ into $AlEt_2Cl$ is most easily accomplished by means of a reaction with $AlEt_3$. It is advisable to ensure that the $AlEt_3$ or the Lewis base is not used in an excess relative to $AlEtCl_2$. As to washing with diluent, this method may be carried out very well already before the β- into γ-conversion is started.

If desired, the process according to the invention can also be used for the preparation of a catalyst-forming composition which contains at least two components of the type described above, in which case the components differ from each other e.g. in that during their preparation the mixing of $AlEt_2Cl$ and $TiCl_4$ took place at a different specific stirring power. Thus, using for example the same equipment, two or more components can be prepared separately, each time at a different stirring speed, and these components can be mixed in a certain ratio. In this way mixtures of catalyst components can be prepared which as far as particle size is concerned contain two or more specific, relatively narrow, fractions. During use in the polymerization this may result in a further improvement of the bulk density of the polymer powder to be prepared.

It is of course also possible to change the stirring speed during the mixing of $AlEt_2Cl$ and $TiCl_4$, but this technique may lead to non-reproducible results.

The polymerization by means of the above $TiCl_3$-containing catalyst components or compositions thereof can be carried out in any manner known per se, that is by using these components or compositions in the presence of an activator, preferably a quantity of $AlEt_2Cl$ such that the final atomic ratio of Al:Ti is 1.5:1 to 10:1.

The use of $TiCl_3$-containing components prepared according to the invention in polymerizations which are carried out with stirring, in the presence of a liquid diluent, also has the great advantage that the polymer suspensions formed permit of easy stirring even at relatively high polymer concentrations. In most cases polymer concentrations of 40—45% by weight are permissible.

If desired the polymerization can take place with the addition of very small quantities of water. As a rule fewer than 10, for example 2—6 parts by weight of water are used per million parts by weight of diluent.

The $TiCl_3$-containing components prepared according to the novel process described above can also be used for carrying out polymerizations in the gaseous phase. If desired the properties of the polymer which are obtained by means of the catalyst components according to the invention can even be further enhanced by an aftertreatment. Thus, these powders can further be subjected to a thermal aftertreatment, for example at 140°C—160°C.

The process according to the invention will now be elucidated by the following Examples.

EXAMPLES.

Tables I to VI refer to a number of experi-

ments (Nos. 1—32) which, unless otherwise specified, were carried out under the following conditions:

The preparation of the titanium-containing catalyst component took place under a nitrogen blanket at atmospheric pressure and with stirring in a reactor with a capacity of 1 litre and a diameter of approximately 9 cm. The reactor had no baffles and was provided with a 6-blade turbine stirrer. The greatest diameter of the stirrer was 5 cm, the distance from the lower side of the stirrer to the bottom of the vessel equalled approximately $\frac{1}{4}$ of the height of the reaction vessel, while the volume swept by the stirrer during stirring amounted to approximately 5% of the internal reactor volume. The reactor, including its cover, was brought to the dosing temperature shown in the Tables and charged at that temperature with a solution of diethylaluminium monochloride in a hydrocarbon fraction which was substantially completely free from water, oxygen and aromatics, contained approximately 33% by weight of 2,2,4-trimethylpentane and over 62% by weight of other octane isomers, and had a boiling range of approximately 100°C—112°C.

The $AlEt_2Cl$-concentration of this solution is shown in the Tables.

With maintenance of the low temperature selected and with continuous stirring at the stirring speed, indicated in the Tables as tip speed, titanium tetrachloride or a solution thereof in the hydrocarbon fraction just mentioned was then gradually added to the reactor contents in such a quantity that the molar ratio selected between 0.5 and 1.2 of the total quantities of diethylaluminium monochloride and titanium tetrachloride used in this mixing step was attained. This molar ratio, the concentration of the titanium tetrachloride added, the time required for the addition of $TiCl_4$ and the specific stirring power at the end of the $TiCl_4$ addition are likewise shown in the Tables. During the addition of $TiCl_4$ the stirring speed remained unchanged; consequently, owing to the smaller liquid volume the specific stirring power at the beginning of this addition was greater than at the end, but as a rule not more than 1.5 times as great.

The temperature of the resulting mixture was subsequently allowed to rise gradually to approximately 40°C, within a specified time and with continuous stirring at unchanged stirring speed, after which this temperature was maintained under the same stirring conditions for a certain, likewise specified time.

Finally, the mixture was transferred to an autoclave with turbine stirrer and heated therein over a certain period to a temperature of 155°C and kept at that temperature for sometime whereupon it was allowed to cool to room temperature. These actions were also carried out in a nitrogen atmosphere with uninterrupted stirring of the mixture at the same stirring speed. The dimensions and the shape of the autoclave and of the stirrer present therein were the same as those of the first reactor and the stirrer present therein. For further data reference is made again to the Tables.

The catalyst component thus obtained was examined microscopically as to size, shape and surface of the particles, and subsequently used as catalyst component in a propylene polymerization which was carried out at 60°C and atmospheric pressure in the fraction of octane isomers referred to previously. For this purpose 15 millimoles of diethylaluminium monochloride were first dissolved in $1\frac{1}{2}$ litres of this diluent, whereupon this solution was saturated at the polymerization temperature with propylene containing a minor amount of hydrogen. The partial propylene pressure was approximately 0.75 atm.abs.

Subsequently, the propylene-saturated solution was mixed with dibutyl ether in an amount just sufficient for complexing approximately 95 mol.% of the quantity of ethylaluminium dichloride present in the catalyst component still to be added. After this an amount of catalyst component was added which corresponded with approximately 5 milliatoms of titanium. The polymerization started immediately and was continued for about 10 hours. During the polymerization the supply of hydrogen was controlled in such a manner that the effluent gas invariably contained 0.7—0.9 vol.% of hydrogen, as a result of which the intrinsic viscosity (I.V.) of the polymer to be prepared, as measured in decaline at 135°C, was invariably approximately 2.9—3.1 dl/g. The polymerization was terminated by introducing nitrogen instead of propylene and by adding to the reaction mixture secondary butanol and gaseous hydrogen chloride. The reaction mixture was then kept at 80°C for some time, whereupon the resulting polymer suspension was successively washed once with a 1% by weight solution of HCl in water and three times with water. After admixture of 0.05% by weight (based on polymer) of 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert.butyl-4-hydroxybenzyl)benzene the suspension was subjected to steam distillation to a maximum temperature of 100°C in the presence of a small amount of Na_2CO_3 (pH = approx. 9), filtered off and dried under nitrogen for 8 hours. The activity of the catalyst component used was expressed as specific polymer-forming rate in g of polymer.(g of $TiCl_3)^{-1}.h^{-1}$. (atm. propylene)$^{-1}$.

Of the polymer thus prepared the I.V. in decaline at 135°C, the percentage of product which could be extracted with boiling diethyl ether, the freely settled bulk density of the resulting polymer powder and the flow properties of this powder were determined.

The determination of the freely settled bulk density was carried out by means of a sheet steel funnel in the form of a truncated cone

with an internal upper diameter of 81 mm, an internal lower diameter of 9 mm and a height of 114 mm and a cylindrical glass receptacle with a volume of approximately 100 ml, an internal diameter of 40 mm and an internal height of 80 mm. The receptacle was tared to the nearest 0.1 g. The lower side of the funnel was at 38 mm above the upper edge of the receptacle. Using a 200 ml measuring cylinder, a quantity of 120 ml of the polymer powder which had previously been passed through an ASTM No. 40 sieve, was introduced into the funnel after the lower side thereof had been closed with a glass strip. This strip was subsequently removed so that the contents of the funnel dropped into the receptacle. When the funnel was empty the upper side of the receptacle was levelled with the glass strip and the receptacle was weighed to the nearest 0.1 g. The volume of the receptacle was established by weighing the latter (again to the nearest 0.1 g) after it had been filled with water at room temperature and by deducting the tare from the weight thus found (the specific gravity of the water being taken as 1). The bulk density of the polymer powder was thus equal to the quotient of the weight in grams and the volume of the receptacle in millilitres. In all cases the values shown in the Tables are the average values of two measurements.

The flow of the polymer powder in sec/litre was determined according to ASTM—D 1182—54.

The results of the experiments are also shown in the Tables.

TABLE I

Effect of stirring conditions										
Molar ratio $AlEt_2Cl/TiCl_4$ 0.75. To the $AlEt_2Cl$ solution, which contained 800 mmoles of $AlEt_2Cl$/litre, was added at -30°C over 4 hours the $TiCl_4$ solution which contained 2000 mmoles of $TiCl_4$/litre. Warming-up time from 30°C to +40°C (linear) : 4 h; time at +40°C : 1 h. Warming-up time from 40°C to 155°C : 1 h; time at 155°C : 1 h; coolong time : 1 h.										
	Stirring conditions		Particles of catalyst component		Specific polymer forming rate g of pol. (g of $TiCl_3$)$^{-1}$. h^{-1} (atm. C_3=)$^{-1}$.	Properties of the polymer				
								polymer powder		
Exp. No.	Tip speed stirrer, m/sec.	Specific stirring power after addition of all $TiCl_4$, Watt/m^3	particle size, μ	shape and surface		I.V., dl/g	ether extract, g/ml	bulk density, g/ml	flow, sec/l
1	0.21	2.2	35—40')	very rough	33	2.9	2.4	0.24	20
2	0.44	16.5	33—37	rough	23	2.9	2.6	0.31	10
3	0.79	86	15—16	smooth pellets	23	2.9	2.5	0.36	8
4a	1.05	200	14—15	do	23	3.0	2.5	0.42	7
4b*)	1.05	200	14—15	do	23*)	2.9	2.3	0.42	7
5	1.30	370	10—12	do	23	2.9	2.4	0.41	7
6	1.96	1000	8—10	do	23	3.0	2.6	0.38	8
7	2.30	1600	8—9	do	22	2.9	2.3	0.37	8
7A	2.61	2900	6—8	do	23	3.1	2.5	0.34	9

*) In this experiment the $AlEtCl_2$ present in the catalyst component was not complexed with dibutyl ether prior to the polymerization but converted for the greater part into $AlEt_2Cl$ by reaction with $AlEt_3$ on the basis of approx. 90 mol.% of the $AlEtCl_2$.

') As well as approx. 20% by weight of very minute particles.

The experiments Nos. 1, 2 and 7A were not carried out in accordance with the invention; they are given for comparison only.

TABLE II

Effect of the $TiCl_4$ and $AlEt_2Cl$ concentration

Molar ratio $AlEt_2/TiCl_4$ = 0.75. $TiCl_4$ or $TiCl_4$-solution added to $AlEt_2Cl$-solution at −30°C over 4 hours. Warming-up and cooling as in Table I. Tip speed of stirrer 0.79 m/sec. Specific stirring power after addition of all $TiCl_4$: 86 Watt/m³.

Exp. No.	$AlEt_2Cl$ conc., mmol/l	$TiCl_4$ conc., mmol/l	Particles of catalyst component: particle size, μ	Particles of catalyst component: shape and surface	Specific polymer-forming rate, g of pol. (g of $TiCl_3$)$^{-1}$ h.$^{-1}$ (atm C_3=)$^{-1}$	Properties of the polymer: I.V., dl/g	Properties of the polymer: ether extract, %w	Polymer powder: bulk density, g/ml	Polymer powder: flow, sec./l
8	500	9150	20—25	smooth pellets	23	2.9	1.8	0.35	8
9	800	9150	15—30	do	25	2.9	1.6	0.40	7—8
10	1600	9150	10—35	do	25	2.9	2.1	0.44	8
11	2600	9150	10—35')	do	23	3.0	2.0	0.36	10
3	500	2000	15—16	do	23	2.9	2.5	0.35	8
13	800	2000	15—16	do	23	2.9	2.5	0.36	8
12	1600	2000	15—35	do	26	2.9	2.3	0.41	7—8

') As well as approx. 5% by weight of very minute particles.

TABLE III

Effect of temperature during the addition of $TiCl_4$												
Molar ratio $AlEt_2Cl/TiCl_4$ = 0.75. $TiCl_4$-solution added to $AlEt_2Cl$-solution over 4 hours. Warming-up and cooling as in Table I												
		Stirring conditions				Particles of catalyst component		Specific polymer forming rate, g of pol. (g of $TiCl_3)^{-1}$ h^{-1}. $(atm.C_3)^{-1}$	Properties of the polymer			
											polymer powder	
Exp. No.	Dosing temp., °C.	tip speed stirrer m/sec.	specific stirring power, Watt/m³	$AlEt_2Cl$ conc. mmol/l	$TiCl_4$ conc., mmol/l	particle size, μ	shape and surface		I.V., dl/g	ether extract, %w	bulk density, g/ml	flow, sec./l
4a	30	1.05	200	800	2000	14—15	smooth pellets	23	3.0	2.5	0.42	7
14	40	1.05	200	800	2000	14—15	do	20	2.9	2.5	0.41	7
10	30	0.79	86	1600	9150	10—35	do	25	2.9	2.1	0.44	8
15	40	0.79	86	1600	9150	14—15	do	25	3.1	0.7	0.41	7—8
3	30	0.79	86	800	2000	15—16	do	23	2.9	2.5	0.36	8
16	20	0.79	86	800	2000	15—16	not completely smooth')	25	2.9	2.5	0.34	9—10
17	3	0.79	86	800	2000	15—16	rough')	26	2.9	2.6	0.30	12
18	3	1.05	200	800	2000	14—15")	rough	27	3.1	2.4	0.20	14
19	−5	0.79	86	800	2000	10—16	rough*)	22	3.0	2.7	0.28	20
20	−5	1.05	200	800	2000	8—15")	rough*)	20	2.9	2.8	0.17	25

') approx. 2% by weight of needle-shaped particles present
") as well as approx. 15% by weight very minute particles
*) as well as approx. 4% by weight or more of needle-shaped particles present.

The experiments Nos. 17—20 were not carried out in accordance with the invention, they are given for comparison only.

TABLE IV

Effect of duration of the $TiCl_4$-addition

Molar ratio $AlEt_2Cl/TiCl_4$ = 0.75. $TiCl_4$-solution added to $AlEt_2Cl$-solution at −30°C. Warming up and cooling as in Table I.

Exp. No.	Stirring conditions: tip speed m/sec.	Stirring conditions: specific stirring power, Watt/m^3	$AlEt_2Cl$ conc., mmol/l	$TiCl_4$ conc., mmol/l	Duration of adding $TiCl_4$, h	Particles of catalyst component: particle size, μ	Particles of catalyst component: shape and surface	Specific polymer-forming rate, g of pol. (g of $TiCl_3$)$^{-1}$ h.$^{-1}$ (atm C_3=)$^{-1}$	Properties of the polymer: I.V., dl/g	Properties of the polymer: ether extract, %w	Polymer powder: bulk density, g/ml	Polymer powder: flow, sec./l
10	0.79	86	1600	9150	4	10—35	smooth pellets	25	2.9	2.1	0.44	8
21	0.79	86	1600	9150	6	20—35')	do	31	3.1	1.9	0.33	8—9
4a	1.05	200	800	2000	4	14—15	do	23	3.0	2.5	0.42	7
22	1.05	200	800	2000	8	14—17	not completely smooth	20	2.9	2.5	0.36	7
23*)	1.35	400	800	2000	4	12—14	smooth pellets	17*)	2.9	2.5	0.38	7—8
24*)	1.35	400	800	2000	1	12—14	do	12*)	3.1	2.6	0.33	8—9
25*)	1.35	400	800	2000	1/8	14—15	do	16*)	3.0	2.4	0.31	10

') as well as approx. 2% by weight of minute particles

*) In these experiments no ether had been added to the catalyst component prior to polymerization.

TABLE V

Effect of the molar ratio $AlEt_2Cl/TiCl_4$

Concentration of $AlEt_2Cl$-solution and $TiCl_4$-solution, temperature and time required for the addition of $TiCl_4$-solution, as well as warming up and cooling as in Table I

Exp. No.	Stirring conditions: tip speed stirrer, m/sec.	Stirring conditions: specific stirring power, Watt/m³	Molar ratio $AlEt_2Cl/TiCl_4$	Particles of catalyst component: particle size, μ	Particles of catalyst component: shape and surface	Specific polymer-forming rate, g of pol. (g of $TiCl_3$)$^{-1}$.h^{-1} = (atm C_3)$^{-1}$	Properties of the polymer: I.V., dl/g	Properties of the polymer: ether extract, %w	Polymer powder: bulk density, g/ml	Polymer powder: flow, sec/l
3	0.79	86	0.75	15—16	smooth pellets	23	2.9	2.5	0.36	8
26	0.79	86	0.95	15—16')	not completely smooth	25	3.1	2.6	0.33	8
27*)	0.92	140	0.75	14—15	smooth pellets	16*)	2.9	2.5	0.38	7—8
28*)	0.92	140	0.53	15—16')	rough	12*)	3.1	2.6	0.32	9—10
4a	1.05	200	0.75	14—15	smooth pellets	23	3.0	2.5	0.42	7
29	1.05	200	0.95	14—15")	not completely smooth	20	3.0	2.4	0.35	8
30	1.05	200	0.53	14—15')	smooth pellets	21	2.9	2.5	0.36	8

') as well as approx. 10% by weight of minute particles
") as well as approx. 20% by weight of minute particles
*) no complexing with dibutyl ether used.

TABLE VI

Effect of increased stirring speed after warming-up to +20°C.

Concentration of $AlEt_2Cl$-solution and $TiCl_4$-solution, temperature during addition of the $TiCl_4$-solution, warming up and cooling as in Table I, except that the time taken to add the $TiCl_4$-solution was 3 hours and the mixture was kept at +20°C — +40°C for 8 hours. No complexing with dibutyl ether used. Molar ratio $AlEt_2Cl/TiCl_4$ = 0.53.

Exp. No.	Stirring conditions: at −30°C and during warming up to +20°C: tip speed stirrer, m/sec	Stirring conditions: at −30°C and during warming up to +20°C: specific stirring power, Watt/m³	Stirring conditions: at +20°C and upwards: tip speed stirrer, m/sec	Stirring conditions: at +20°C and upwards: specific stirring power, Watt/m³	Particles of catalyst component: particle size, μ	Particles of catalyst component: shape and surface	Specific polymer-forming rate, g of pol. (g of $TiCl_3$)$^{-1}$.h^{-1} = h^{-1}.(atmC_3)$^{-1}$	Properties of the polymer: I.V., dl/g	Properties of the polymer: ether extract, %w	Properties of the polymer: Polymer powder: bulk density g/ml	Properties of the polymer: Polymer powder: flow, sec/l
31	0.92	140	0.92	140	15—16	moderately smooth	8	3.0	2.6	0.34	7—8
32	0.92	140	1.30	370	15—16	smooth pellets	9	3.0	2.5	0.38	7—8

Table VII below shows the results and some test conditions of a range of experiments (Nos. 33—45) which, except for the following differences, were conducted as described with reference to Tables I—IV. The differences consisted in that the catalyst component was prepared in n-decane as diluent and that the polymerization took place in 2,2,4-trimethyl pentane at 75°C.

TABLE VII

Preparation of catalyst component in n-decane								
$AlEt_2Cl$-concentration = 2000 mmol/l; $TiCl_4$-concentration = 2000 mmol/l; tip speed of stirrer 0.79 m/sec.; specific stirring power after addition of all $TiCl_4$: 86 Watt/m³, time of standing without heat or cooling being applied after mixture had been warmed up to +20°C : 1 h; warming-up time from 20°C to 155°C : 1 h; time at 155°C : 1 h; cooling time : 1 h.								
					Properties of the polymer			
							Polymer powder	
Exp. No.	Dosing temp., °C.	molar ratio $AlEt_2Cl$/$TiCl_4$	Duration of $TiCl_4$-addition, h	Duration of warming up to +20 °C, h	I.V., dl/g	ether extract, %w	bulk density, g/ml	flow sec/l
33	—10	0.95	½	1	2.9	3.5	0.34	9
34	—10	0.95	11	1	2.9	3.3	0.38	7—8
35	—10	0.95	2	1	3.1	3.2	0.39	7
36	—10	0.95	3	1	3.0	3.2	0.40	7
37	—10	0.95	4	1	2.9	3.4	0.35	8
38	—10	0.95	2	2	3.0	3.3	0.39	7—8
39	—10	0.95	2	3	2.9	3.3	0.34	8
40	—20	0.95	3	1	3.0	3.5	0.36	8
41	—30	0.95	3	1	3.1	3.2	0.39	7—8
42	—20	0.85	3	1	3.0	3.2	0.40	7
43	—10	0.75	3	1	2.9	3.1	0.40	7
44	—20	0.75	3	1	3.0	3.4	0.36	8
45	—10	0.50	3	1	3.1	3.5	0.35	8

Table VIII refers to a number of experiments (Nos. 46—51 in which the catalyst component was prepared in various paraffinic diluents at −30°C. The molar ratio $AlEt_2Cl$: $TiCl_4$ was 0.75:1, the time taken to add $TiCl_4$ was 4 hours and the duration of warming-up to +20°C was 2 h. Except for $AlEt_2Cl$-concentration and $TiCl_4$-concentration, the conditions were the same as shown in Table VII. The polymerizations were carried out in 2,2,4-trimethyl pentane at 70°C.

TABLE VIII

Preparation of the catlayst component in various diluents							
				Properties of the polymer			
Exp. No.	Diluent	$AlEt_2Cl$ conc., mmol/l	$TiCl_4$ conc., mmol/l	I.V., dl/g	ether extract, %w	bulk density, g/ml	flow sec./l
46*)	n-decane	2000	2000*)	3.2	3.3	0.36	8
74	2,2,4-trimethylpentane	800	2000	3.0	3.2	0.41	7—8
48	n-hexane	800	2000	2.9	3.0	0.42	7
49	n-pentane	800	2000	3.1	3.1	0.43	7
50	n-pentane	564	9100	2.9	2.6	0.42	7
51	n-butane	564	9100	3.0	2.5	0.40	7—8

*) in this experiment the time taken to add $TiCl_4$ was 3 h, the duration of warming up to +20°C: 1 h.

Table IX shows the data and results of a pilot-plant experiment (Exp. No. 52) in which the catalyst component was prepared in two stirred 10-litre reaction vessels each with a diameter of 20 cm, and the polymerization of propylene was carried out continuously at elevated pressure in a stirred 95-litre vessel containing 60 litres of reaction mixture. The stirrers in the 10-litre vessels were 6-blade turbine stirrers with a greatest diameter of 10 cm, while the volume swept by the stirrers in these vessels during stirring was again approximately 5% of the internal reactor volume. In the case of the 10-litre reactors the distance between the lower side of the stirrer and the bottom of the vessel was again equal to ¼ of the height of the vessel. Also in this case the $TiCl_4$ was added to the $AlEt_2Cl$. Before introduction of the $AlEt_2Cl$ into the first 10-litre vessel this vessel, including its cover, was cooled to the temperature at which the subsequent addition of $TiCl_4$ was to take place. The $AlEt_2Cl$ was supplied to this vessel at such a low rate that the temperature within the vessel temporarily rose a few degrees only. During the preparation of the catalyst component and during the polymerization the diluent was the same as used in experiment Nos. 1—32.

The conversion of the β-modification of the $TiCl_3$-containing catalyst component into the γ-modification took place in the second 10-litre reaction vessel which was designed as an autoclave. Before this conversion was brought about the β-modification was washed three times with the just-mentioned diluent at ambient temperature.

TABLE IX

Pilot-plant experiment	
Preparation of catalyst component:	
Tip speed of stirrer in both 10 litre reactors	1.73 m/sec.
Specific stirring power after addition of all $TiCl_4$	350 Watt/m^3
Molar ratio $AlEt_2Cl/TiCl_4$	0.75
$AlEt_2Cl$-concentration	800 mmol/l
$TiCl_4$-concentration	2000 ,, ,,
Temperature during $TiCl_4$-addition	—30°C
Duration of $TiCl_4$-addition	4 h
Duration of warming-up to +40°C	4 h
Time at —40°C	1 h
Duration of warming-up to 155°C (in second 10-litre reactor)	1 h
Time at 155°C.	1 h
Duration of cooling to —20°C	1 h
Shape and surface of resultant particles	smooth pellets
Particle size	12 — 14 μ
Continuous polymerization	
Pressure	6 atm. abs.
Partial propylene pressure	5.4 atm. abs.
Hydrogen content of gas cap	1.8%v
Temperature	60°C
Average residence time	10 h
$TiCl_3$-concentration	2.3 mmol/l
Molar ratio $AlEt_2Cl/TiCl_3$	4 : 1
Polymer-forming rate	19 g of pol. (g of $TiCl_3)^{-1}$. $h.^{-1}$ Catm. $\overline{\overline{C_3}})^{-1}$

Pilot-Plott experiment	
Polymer concentration in reactor	40%w.
Properties of resultant polymer	
I.V.	2.9 dl/g
Material capable of being extracted with boiling diethyl ether	2.9%w
Bulk density of the powder	0.45 g/ml
Flow of the powder	5 — 6 sec/l
Tensile strength	360 kg/cm²

WHAT WE CLAIM IS:—

1. A process for the preparation of a catalyst component suitable for the polymerization of α-olefins having up to six carbon atoms to polymer powders with improved bulk density and flow properties, which process comprises (1) mixing diethylaluminium monochloride and titanium tetrachloride at a temperature below −5°C in a molar ratio within the range of 0.5:1 to 1.2:1 in a paraffinic diluent which is substantially free of oxygen in a reaction vessel whose contents are stirred at a specific stirring power within the range of 50 to 2000 Watt/m³ and (2) subsequently increasing the temperature of the mixture to at least +15°C whilst stirring is continued at a specific stirring power which is kept within the same range at least as long as the temperature is still below +15°C.

2. A process according to claim 1, in which the temperature of the mixture is increased from below −5°C to a value within the range of 70 to 200°C and subsequently lowered to ambient temperature below 70°C whilst stirring is continued at a specific stirring power which no longer needs to be within the range of 50 to 2000 Watt/m³ as soon as the temperature is above +15°C.

3. A process according to claim 1 or 2, in which the reaction vessel is unbaffled.

4. A process according to any one of the preceding claims in which the contents of the reaction vessel are stirred with an agitator sweeping a volume of less than 10% of the internal vessel volume and rotating with a tip speed of more than 0.5 meter per second.

5. A process according to claim 4, in which the agitator is a turbine stirrer.

6. A process according to any one of the preceding claims in which the titanium tetrachloride and the diethylaluminium monochloride are mixed at a substantially constant temperature above −45°C and in a gradual manner so as to attain the molar ratio of 0.5—1.2 in at least one hour but at most eight hours.

7. A process according to any one of the preceding claims in which the average increase rate of the temperature of the mixture within the range of −45°C to +45°C is at most 1.5°C per minute.

8. A process according to claim 7, in which the average increase rate of the temperature within the range of −45°C to +45°C is at least 0.1°C per minute.

9. A process according to any one of the preceding claims in which the titanium tetrachloride and the diethylaluminium monochloride are mixed at a temperature within the range of −10°C to −40°C.

10. A process according to any one of the preceding claims in which the vessel is cooled down to the temperature below −5°C before diethyl-aluminium monochloride or titanium tetrachloride is introduced.

11. A process according to any one of the preceding claims in which the diethylaluminium monochloride is introduced first, whereupon the titanium tetrachloride is added to the diethylaluminium monochloride.

12. A process according to any one of the preceding claims in which the molar ratio for mixing the diethylaluminium monochloride and the titanium tetrachloride is within the range of 0.65:1 to 0.85:1.

13. A process according to any one of the preceding claims in which both the titanium tetrachloride and the diethylaluminium monochloride are used in a concentration of more than 500 millimoles per liter.

14. A process according to claim 13, in which the diethylaluminium monochloride concentration is less than 1800 millimoles per litre.

15. A process according to any one of the preceding claims in which the paraffinic diluent is an alkane with 4—10 carbon atoms.

16. A process according to any one of the preceding claims in which the specific stirring power is within the range of 80 to 800 Watt/m³ at least as long as the temperature of the mixture is below +15°C.

17. A process according to any one of the preceding claims in which the stirring speed is kept substantially constant at least as long as the temperature of the mixture is below +15°C.

18. A process according to any one of the preceding claims in which the stirring conditions to be applied at temperatures below +15°C are maintained up to a temperature between +15°C and +70°C.

19. A process according to any one of claims 1—17 in which at a temperature between +15°C and +45°C the specific stirring power is increased.

20. A process according to any one of the preceding claims in which the temperature of the mixture is kept between +15°C and +45°C for at least ¾ hours.

21. A process according to claim 20, in which the temperature of the mixture is kept between +15°C and +45°C for at least two hours.

22. A process according to any one of the preceding claims in which monoethylaluminium dichloride, formed during reaction of diethylaluminium monochloride and titanium tetrachloride, is removed from the mixture or converted into diethylaluminium monochloride or into a complex.

23. A process according to claim 22, in which the monoethylaluminium dichloride is complexed with the aid of a Lewis base.

24. A process for the preparation of a catalyst component according to any one of the preceding claims substantially as described hereinbefore with special reference to experiments Nos. 3—7, 8—16 and 21—52 of the Examples.

25. A catalyst component whenever prepared by a process according to any one of the preceding claims.

26. A catalyst composition comprising at least one component according to claim 25.

27. A catalyst composition comprising at least two catalyst components according to claim 25, the components differing in that they have been prepared by mixing the diethylaluminium monochloride and the titanium tetrachloride at different specific stirring powers.

28. A process for the polymerization of α-olefins having up to six carbon atoms to polymer powders with improved bulk density and flow properties in which process a catalyst component according to claims 25 or a composition according to claim 26 or 27 is used in the presence of an activator.

29. A process according to claim 28, in which the number of carbon atoms of the α-olefins is up to three.

30. A process according to claim 29 in which propene is used as an α-olefin and the final heat treatment during the preparation of the catalyst component(s) is carried out at a temperature within the range of 100—200°C.

31. A process according to any one of claims 28—30 in which the catalyst component according to claim 25 or the composition according to claim 26 or claim 27 is used in the presence of diethylaluminium monochloride, the final atomic ratio of Al:Ti ranging from 1.5:1 to 10:1.

32. A polymerisation process according to any one of claims 28—31 substantially as described hereinbefore with special reference to experiments Nos. 3—7, 8—16 and 21—52 of the Examples.

33. Polymer powders whenever prepared by a process according to any one of claims 28—32.

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